

Synergistic Hypergolic Ignition of Amino End Group in Monomers and Polymers

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Abstract. A few monomers, oligomers and polymers with amino end groups have been discovered to undergo synergistic ignition with red fuming nitric acid (RFNA) when mixed with large quantities of magnesium powder. Aluminium powder under similar conditions does not ignite the mixture while powders of **Zn, Co** and **Cu** cause the ignition. Amongst the polymers used in the experiment commercially available nylon 6 is the most important which may be used as a binder for rocket propellant fuel grains, hypergolic with RFNA. Degree of polymerisation or the chain length **of the polymers does not drastically** affect the synergistic ignition of the polymer mixture with magnesium powder but high molecular weight and fully aromatised polymers like Kevlar and Nomex fail to ignite under similar conditions. Based upon the earlier work **of the authors**, explanations for the phenomena **observed** have **been** provided in terms of creation of hot spots leading to ignition at the amino end groups.

1. Introduction

Synergistic hypergolicity of solid aromatic primary **amines** and diamines mixed with large quantities of magnesium powder with RFNA as oxidizer' is reported. **The** present work is aimed at rendering high molecular weight commercial polymers like nylon 6 and nylon 66 hypergolic with RFNA **which** has **been considered impossible** in the past. We have now discovered that though nylon 6 and nylon 66 do not ignite with RFNA or **N₂O₄**, spontaneous ignition can be achieved if the polymers are mixed with finely divided magnesium powder in various quantities. Hence we felt it worthwhile to extend our experiment to solid monomers, oligomers and **polymers** having -NH₂ end group in general as it can form an easy but elegant test for the group irrespective of the solubility of the parent substance in addition to the oligomers and the polymers forming hypergolic fuels for hybrid rocket motors.

2. Experimental

2.1 Materials

Nylon 66 with mp. 265°C was synthesised after Braun² et al. The dihydrazides and the polymeric Schiff bases were prepared after Volvelskii³ et al. and Delman⁴ et al. respectively. These workers have reported the characterization of their products which contained terminal $-\text{NH}_2$ groups.

Nylon 6 was used in small pieces cut from commercial fabrics obtained from M/s Garware Nylons, Pune.

Two hardners for epoxy resins such as aniline-formaldehyde linear condensation product (AFC-M/4) and the condensation product of dimerized linseed oil and an aliphatic polyamine (No 771) were obtained from Dr Beck & Co India Ltd in viscous packs and used as such.

2.2. Methods

2.2.1 ID Measurements

ID values were measured in a modified Pino's apparatus as described by Kulkarni & Panda⁵ earlier where an electrical pulse is fed to an electronic timer to start it. Fuel and oxidizer coming in contact with each other produce a flame that sends a stop pulse through a photo cell for the timer. Delays thus recorded are averaged over several values to give the mean ID and its scatter in terms of standard deviation.

The solid amino compounds were powdered which passed through a 100 mesh sieve but were retained in a 150 mesh sieve (dia $149\text{--}105\mu$). Similar restriction of size was not possible for nylon 6 and nylon 66 and viscous amino hardners for epoxy resins. Nylon 6 was used in small pieces cut from commercial fabric whereas nylon 66 and amino hardners for epoxy resins were mixed with magnesium powder with the help of a mortar and pestle as thoroughly as possible.

Magnesium powder was of type 5 as described by an Indian Standard (6). It contained non-coated powders of assorted sizes which passed through a 150 mesh sieve.

RFNA used) in the measurements had 2 I per cent N_2O_4 , 76 per cent HNO_3 , and 3 per cent H_2O .

3. Results and Discussions

Some of the solid dismino monomers like p-phenylenediamine, p-benzidine and hexamethylenediamine are themselves hypergolic but several others like m-phenylenediamine p, p'-diaminodiphenylmethane are not hypergolic with RFNA. In either cases the compounds turn highly hypergolic when mixed with about 70 per cent by

weight of magnesium powder. The details of this work is already given in an earlier **communication**¹. Since then we have tested similar mixtures of a number of **amino-phenols**, **aminoacids**, **dihydrazides**, **polymeric Schiff bases**, **polyamides (nylons)** and **viscous polymeric amino hardners** for epoxy resins with magnesium powder. These compounds with amino end groups were **characterised** by elemental analysis and IR spectral **measurements**. A spontaneous ignition was achieved for their mixtures with magnesium powder, whether they were themselves hypergolic or otherwise, using RFNA as oxidizer. Details of the ignition delay values measured are reported in Table 1.

It can be seen from Table 1 that there is no fixed percentage of magnesium at which different compounds produced a minimum ignition delay. This occurred at 40 per cent of Mg for compound No 2, 4 and 5; 50 per cent of Mg for compound No 7 and 9; 60 per cent of Mg for compound No 1, 3, 8 and 13; 70 per cent of Mg for compound 6, 10, 11, 14 and 15 and 80 per cent of Mg for compound 12. However, 70 per cent of Mg in a mixture was chosen to study the effect of 1 per cent NH_4VO_3 dissolved in RFNA on ID as an oxidation catalyst to make it fall in line with our earlier work¹. In all case there was a decrease in ID when RFNA mixed with NH_4VO_3 was used indicating oxidation to be one of the most important pre-ignition reactions in addition to the usual acid-base neutralisation and nitration.

The importance of oxidation at the preignition stage becomes obvious when fully **aromatised polymers** with **amino end groups like** Kevlar and Nomex mixed with **magnesium powder** fail to become hypergolic with RFNA. Easy oxidation of **polymeric backbone** looks to be an essential condition for synergistic ignition in the systems studied by us.

This restriction does not apply to low polymeric compounds like the poly Schiff bases containing reactive $>\text{C}=\text{N}$ bonds in their backbones.

Role of magnesium powder in our study is interesting. It reacts vigorously with HNO_3 , N_2O_4 and H_2O , the different constituents of RFNA though remaining non-hypergolic. The most crucial reaction for ignition of the mixture of amino compounds with magnesium seems to be the interaction of the metal and its nitrate with the initial reaction intermediates of the primary amino groups with HNO_3 . Strong bases like tertiary and Schiff bases without amino end groups mixed with magnesium powder do not produce synergistic ignition with RFNA. They form salts almost quantitatively with HNO_3 , like

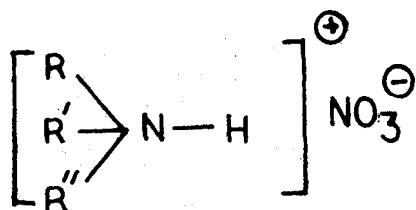


Table 1. Ignition delay values of monomers and polymers with amino end groups mixed with magnesium powder with RFNA as oxidizer

Compound	M.P.	Ignition delay ^a values in milliseconds								Minimum % of Mg. (type 5) in the fuel for hypergolicity
		percentage of Mg powder (type 5) in the fuel								
		0	40	50	60	70	80	100		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Hydrazine and glyoxal (1 : 1) condensate	>300	Mean Standard deviation	205.1 6.6	76.8 2.0	72.2 0.7	66.6 3.0	78.6 2.6	91.9 2.7	75.8 1.6	—
Ethylenediamine and glyoxal (1 : 1) condensate	>300	Mean Standard deviation	Hyper-golic with long delay	25 3.0	450.3 6.1	457.6 4.1	559.6 8.08	966.3 9.2	646.6 1.5	—
Hexamethylenediamine and glyoxal (1 : 1) condensate	>300	Mean Standard deviation	Non-hyper-golic	930 6.6	508.6 3.5	419.3 4.4	949.6 6.5	985.9 11.1	940.4 2.5	5
p-Phenylenediamine and glyoxal (1 : 1) condensate	>300	Mean Standard deviation	Hyper-golic with long delay	60.7 0.7	71.0 1.2	88.3 3.2	107 3.8	112.6 4.0	103 1.6	—
m-Phenylenediamine and glyoxal (1 : 1) condensate	>300	Mean Standard deviation	755.3 8.0	56.3 3.7	75.6 2.3	264.6 3.0	353.6 3.1	410.6 3.5	345.6 2.1	—
p,p'-Diaminodiphenyl methene and glyoxal (1 : 1) condensate	>300	Mean Standard deviation	Non-hyper-golic	Igni-tion with long delay	1282.3 10.5	1121.6 25.1	855 6.4	Igni-tion with long delay	827.2 5.6	25

(Contd.)

Table 1. (contd.)

1	2	3	4	5	6	7	8	9	10	11
<i>p</i> -Benzidine and glyoxal (1 : 1)	>300	Mean Standard deviation	Hyper-golic, long delay	165.3 1.31	98.5 2.0	149.6 2.1	198.3 2.5	224.3 3.1	190.3 2.7	—
Dihydrazide of oxalic acid	219	Mean Standard deviation	Hyper-golic, long delay	85.3 3.0	79.3 3.5	64 1.0	73.3 2.1	113.3 1.0	70 1	—
Dihydrazide of malonic acid	155	Mean Standard deviation	Hyper-golic, long delay	281.3 3.5	157.6 3.1	180.3 1.5	271 3.0	279.6 2.1	267.7 2.1	—
Dihydrazide of succinic acid	168	Mean Standard deviation	Hyper-golic, long delay	360.3 4.0	252.3 3.5	225 2.6	212.3 3.1	215.6 1.5	204.3 3.1	—
Dihydrazide of adipic acid	171	Mean Standard deviation	Hyper-golic, long delay	321.6 3.2	279.3 1.5	236.3 4.0	215.6 3.1	248.3 3.5	201 2.0	—
Nylon 6	215	Mean Standard deviation	Non-hyper-golic	Ignition with long delay	3643.5 43.1	1168.6 29.9	622 44.2	533.3 3.7	562 4.2	5

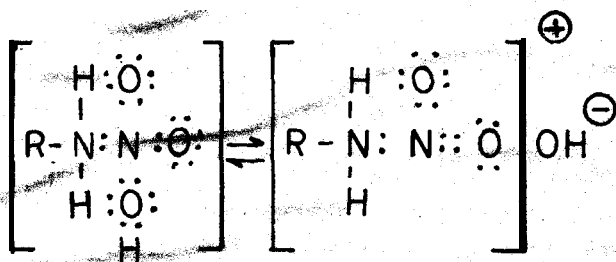
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Table 1. (contd.)

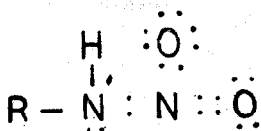
1	2	3	4	5	6	7	8	9	10	11
Nylon 6. 6	265	Mean Standard deviation	Non- hyper- golic	igni- tion, long delay	3225.5 38.8	1142.3 29.5	1332.3 12.5	non- hyper- golic	1274 8.4	20
Aniline formaldehyde linear condensation product (AFC-M/4)	—	Mean Standard deviation	Hyper- golic long delay	igni- tion, long delay	1134 19.7	870.5 20.5	345.6 30.4	481 22.8	311 9.8	—
Dimerized linseed oil condensed with polyaniline (no. 771)	—	Mean Standard deviation	Non- hyper- golic	igni- tion, long delay	1260 14.1	1033 12.1	560.5 14.8	709 12.7	527.5 1.0	10

a-Oxidizer to fuel ratio by weight used for the measurements was 1 : 1 which gave minimum ID in all cases.
 b-RFNA used contained ammonium metavanadate (1% by weight) as catalyst.

where the acidic H atom remains strongly bound to the amino nitrogen. Weak bases like the organic primary **amines** react with HNO_3 , producing Hantzsch complex of the type,



which can eliminate a molecule of water in presence of dehydrating agents to form a nitramine of the structure :



Magnesium and its **nitrate** can **catalyse** the nitramine formation by abstracting water from the Hantzsch complex. For this, experimental evidences have been provided by us earlier. Primary nitramines being thermally unstable decompose producing combustible gases for ignition. Initiation of ignition in the gaseous phase looks to be assisted by vapourisation of magnesium (BP, 1107°C) as a large amount of **MgO** smoke is produced in the flame and the ignition is inhibited by replacement of magnesium with aluminium which boils at 2494°C . This is supported by Coffin⁸ who observed that burning of magnesium ribbon was predominantly a vapour phase phenomenon catalysed by traces of water. Besides, we also found that metal powders with relatively low melting and boiling points like zinc and lead could cause synergistic ignition of solid organic primary amines with RFNA while high melting and boiling metals like iron, nickel, titanium and tungsten fail to produce ignition presumably -due to the difficulty in reaching the gaseous phase. However, further investigation became necessary as the powders of copper and cobalt with high melting and boiling points replacing magnesium in the above fuel mixtures could ignite them with RFNA as well. It was first thought that like magnesium nitrate (anhydrous), nitrates of cobalt, copper and zinc could abstract water from the Hantzsch complex formed by the amines with HNO_3 , thus catalysing the nitramine formation in the synergistic hypergolic reaction. To test this hypothesis freshly prepared aniline nitrate was mixed with powders of cobalt, copper and zinc in 50 : 50 weight proportions and rubbed with slight moisture in a mortar and pestle. There was neither any heat generation nor gas evolution. It may be pointed out that similar mixtures with magnesium underwent rapid exothermic reactions with liberation of nitrous fumes and occasional incidence of fire when rubbed with moisture. It indicates that the mechanism operating for the

synergistic ignition of solid primary **amines** mixed with magnesium powder and RFNA cannot be extended to similar mixtures with cobalt, **copper** and zinc.

Like magnesium, zinc reacts with HNO_3 and H_2O of RFNA to produce hydrogen which is highly combustible. But cobalt and copper do not **liberate hydrogen** either from H_2O or HNO_3 .

It is, therefore, possible that unlike magnesium nitrate, nitrates of cobalt and copper may undergo **complex formation with primary amino group** liberating heat in the preignition stage. These, hydrated nitrates of cobalt, copper, zinc and magnesium were mixed with molten o-nitroaniline, as a representative compound having a comparatively lower melting point for studying the possible interactions between the amino group and the metal ions at elevated temperatures. Incidentally, o-nitroaniline when mixed with magnesium, zinc, cobalt and copper undergoes synergistic ignition with RFNA and thus is a good choice for model reactions. The melts of o-nitroaniline the hydrated metal nitrates of cobalt and copper, zinc and magnesium (1:1 by weight) were cooled down and their far infrared spectra were recorded at the room temperature. It was observed that where as $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ produced simple combination spectra mixed with o-nitroaniline, similar mixtures of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ produced distinctly different spectra than their individual components. As the far infrared region is specific for absorption due to the complex formation of cobalt and copper with the amino ligands⁹, our observations led us to believe that the exothermic complex forming reactions at the preignition stage between the ions of cobalt and copper with primary amino groups might abet synergy in ignition of the mixtures studied by us with RFNA as oxidizer.

3.1 Effect of Chain Length on ID

It may be seen from Table 1 that chain length of polymers which are very small for polymeric Schiff bases (Compound Nb. 1-7, $\overline{DP} = 4$), dihydrazides (compound No. 8-11, $\overline{DP} = 1$) and polymeric amino hardners for epoxy resins (compound No. 14, $\overline{DP} = 6-7$, compound No. 15, $\overline{DP} = 2$), and large for nylon 6 and nylon 66 (compound No. 12 and 13, $\overline{DP} = 200$) do not affect ID drastically as long as the amino end groups exist in them. Fast and exothermic reactions with RFNA taking place at the amino end groups lead to ignition. This supports the concept of creation of hot spots in non-conducting solids as a condition for thermal ignition. Depolymerization which is endothermic does not seem to affect significantly synergistic ignition of polymers studied by us.

4. Conclusion

Synergistic ignition of monomers, oligomers and polymers with NH_2 end groups mixed with various quantities of magnesium powder using RFNA as oxidizer has been discovered. This may help in designing hybrid rocket fuel grains which are hypergolic

-with RFNA and possess desired mechanical strength to prevent erosive burning. It is also observed that Zn, Cu and Co can replace Mg in the fuel mixtures to produce synergistic ignition with RFNA, though through a different mechanism. Hot spot formation at the terminal $-NH_2$ group due to chemical reactions may form the site of initiation of the synergistic ignition phenomenon. This may form a test for $-NH_2$ group in organic substances including oligomers and polymers.

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